ANALYSIS OF STOCK TONICS

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I. Introduction and Purpose.

In recent years the problem of securing an adequate tonic for the most common of stock diseases has attained considerable importance. At the present there are a large number of so-called stock remedies on the market, claiming the ability to cure various types of diseases.

The purpose of this investigation is to analyse as many of the more common tonics as possible in order to determine the principle and most common ingredients and to establish a general system of analysis of the various forms of such tonics. An endeavor was also to be made to formulate a list of the substances analysed and their medicinal value. A review of the literature failed to reveal any work which had been done of this nature. In order to establish a general system of analysis it was deemed necessary to try different methods of analyses and to determine by experiment which method gave the most accurate results in the easiest and quickest manner.

II. Experimental.

The manufacturer of stock tonics usually puts up his preparations for the market in various forms. Some are as powders, mechanically mixed, others as a liquid with water as the usual solvent, while many are pressed in the form of a salt block. It was the aim of the writer to investigate at least two of each type. Instead of giving the trade name of the stock tonics analysed, they are labelled as Sample #1, #2, etc.

Sample #1.

This stock tonic was of the powder type, mechanically mixed, black in color and was one of the most common of the powder form. A qualitative determination of the ingredients showed that it was composed of the following substances.

1. Charcoal (ground)
2. Sodium sulphate
3. Moisture

The charcoal was determined quantitatively as insoluble matter by simply dissolving a five gram sample in water and filtering off the insoluble charcoal in a weighed Gooch crucible and washing with water several times. The filtrate was then used for the determination of the sodium sulphate. The usual method of precipitation with Barium Chloride was used and precipitate allowed to settle and then filtered through a weighed Gooch crucible, dried and weighed.

The moisture determination was made in the usual manner by weighing out five grams and placing the weighing bottle in an oven for an hour at 105° C.

An microscopic examination was made of the water insoluble residue to determine if seeds, roots, or barks were present. Several slides were made with the insoluble residue and on close examination the only substance that seemed to be present was the charcoal.

The following results of this analysis are as follows:

Results:

Moisture.....	42.40%
Sodium Sulphate.....	48.63%
Insoluble Matter....	8.96%
Total.....	99.99%

Calculation on a dry basis:

Sodium Sulphate.....	84.44%
Insoluble Matter....	15.55%
	99.99%

Sample #2.

This stock tonic was of the powder form. A short qualitative was run with the results that the following substances were found; charcoal, free sulphur, sulphates, and small seeds.

Quantitative Methods.

Sulphates were determined in the usual way with Barium Chloride.

Carbon Disulphide extraction by means of the Soxhlet extractor was used for the determination of free sulphur .

Moisture was determined in the usual way.

The insoluble matter including the seed was determined by dissolving a five gram sample in water and then filtering through a weighed Gooch, dried, and weighed.

Under the supposition that the seed was a species of the wormseed, an attempt was made to extract any alkaloid present. The standard method of alkaloidal extraction according to Autenreith and Warren was carried out.

(Autenreith and Warren "Detection of Poisons")

After the final step of the procedure was finished, tests with the various alkaloidal reagents such as Mercury Chloride, Iodo-Potassium Iodide, Potassium Mercuric Iodode were made without result. The method was again carefully repeated and, as in the former case, a negative result was obtained. It was decided that the seed had really no medicinal value and its use was simply as a filler to give weight to the tonic.

The analysis showed the following results:

Sodium Sulphate.....	42.08%
Free Sulphur.....	6.18%
Moisture.....	6.84%
Insoluble Matter....	45.02%
(charcoal, seed)	
	100.12%

Analysis on dry basis:

Sodium Sulphate.....	45.17%
Free Sulphur.....	6.63%
Insoluble Matter....	48.32%
	100.12%

Sample #3.

Since the fact that many of the stock tonics contain many similar constituents, one is able to almost identify their composition with the eye. The next sample analysed showed the presence of iron, sulphate, free sulphur and silica.

Quantitative Methods.

Free sulphur was determined by extraction with Carbon Disulphide in the Soxhlet.

Iron in the form of Ferric Oxide was determined as in Sample #5.

The usual method of determining sulphates with Barium Chloride was used for Sodium Sulphate.

The percentage of Silica was obtained by the method given under Sample #7.

Moisture was determined in the usual way.

The following results were received:

Free Sulphur.....	.149%
Iron as Fe.....	.35 %
Sodium Sulphate.....	60.11 %
Silica.....	11.91 %
Insoluble Matter,...	14.78 %
Moisture.....	13.56 %
Total.....	100.96 %

Analysis on dry basis:

Free Sulphur.....	.172%
Iron as Fe.....	.405%
Sodium Sulphate.....	69.54 %
Silica.....	13.78 %
Insoluble Matter...	17.09 %
	100.987%

Sample #4.

The next sample to be analysed was perhaps one of the most prominent of the stock tonics on the market. It advertised the following compositions; 1-Sulphate of Iron 2-Charcoal 3-Carbonized Peat 4-Sodium Chloride 5-Magnesium Chloride 6-Epsom Salts 7-Quassia Root 8-Tobacco 9-Gentian Root. Many of these substances have a medicinal value and the substance should be of high value as a tonic.

Quantitative Methods.

Percentage of moisture obtained in the usual way.

Ferrous Iron was determined by the Zimmermann-Reinhardt method described in Sample #5.

Total Chlorides were determined by the Fr. Mohr method described in Sample #5.

Total Sulphates were obtained by the Barium Chloride method.

Free Sulphur was determined by the Carbon Disulphide method of extraction.

The method of B. Schmitz# was used for the determination of Magnesium.

(Treadwell and Hall "Analytical Chemistry" Vol.II P. 67)

A five gram sample of the tonic was weighed out and dissolved in hot distilled water. The solution was then filtered and filtrate made slightly acid with dilute Nitric Acid. Crystals of Ammonium Nitrate were then added and solution heated to boiling and then treated with an excess of Sodium Phosphate. One third the volume of 10% Ammonium Hydroxide was at once added and solution allowed to stand for several hours.

The precipitate was then filtered through a weighed Gooch and washed with 3% Ammonium Hydroxide, dried and ignited slowly over a Bunsen flame and finally ignited to a white powder in a Muffle furnace. After cooling the Magnesium Pyro-Phosphate was weighed.

Quassia shavings were mechanically separated and found to be present in a very small amount. The shavings were macerated in a few c.c. of hot water and on testing the extremely bitter taste of Quassia was received.

Gentian and Tobacco were found to be present in a very minute amounts and were not determined quantitatively. The microscope was also used as an aid in the detection of these three substances.

In the calculation, Sodium Chloride and Magnesium Chloride, Magnesium Sulphate and Iron Sulphate were calculated indirectly. Knowing the total percentage of Sulphate and the percent Iron, the percent Iron Sulphate was calculated in the following manner:

$Fe : SO_4 :: \%Fe : X$ X=%Sulphate used as Iron Sulphate.

$\frac{Fe\ SO_4}{Fe} \times \%Fe = \%Fe\ SO_4$

Subtracting the amount of sulphate used as $FeSO_4$ from the total sulphate gave the sulphate to be used as $MgSO_4$.
The percent of Magnesium being determined, the percent of $MgSO_4$ was found in the following manner:

$Mg : SO_4 :: X : \%$Sulphate to be used as $MgSO_4$.
X=% of Mg. to be used as $MgSO_4$.

$\frac{MgSO_4}{Mg} \times \%$ of Mg. to be used= $\%MgSO_4$.

In a similar manner Magnesium Chloride and Sodium Chloride were calculated.

The following results were obtained:

Moisture	.796%
Insoluble Matter (charcoal, peat, and roots)	4.37 %
Free Sulphur	1.942%
Iron Sulphate	1.469%
Magnesium Sulphate	.589%
Magnesium Chloride	.835%
Sodium Chloride	89.67 %
Total	100.627%

Sample #5.

This tonic was of the salt block type. It was light brown in color and of a salty taste. In water solution it was neutral to litmus.

A qualitative test was run to determine the composition. Effervesence upon the addition of dilute Hydrochloric Acid proved the presence of Carbonates. On the addition of Silver Nitrate and Nitric Acid to the water solution, the characteristic test for chlorides was obtained. The presence of the Sulphate was obtained by the use of Barium Chloride. Iron was found on the addition of Hydrochloric Acid and then Ammonia, and a blood red coloration with KCNS denoted the ferric salt. Sulphur was found present in the free state on the addition of a little dilute Hydrochloric Acid and the dry powder on a silver coin.

Quantitative Methods.

Sodium Chloride was determined by the Fr. Mohr's method#.

(Schimpf's "Volumetric Analysis" P171)

A five gram sample of the tonic was weighed out, dissolved in water, filtered and titrated with factor $\frac{N}{10}$ normal Silver Nitrate using Potassium Chromate as an indicator.

The ferric salt was determined as follows: five grams of the tonic was dissolved in dilute Hydrochloric Acid, filtered, a few c.c. Bromine water added and boiled for five minutes. On cooling, Ammonia was added until solution was alkaline and Ferric Hydroxide precipitated, filtered and washed. The Ferric Hydroxide was redissolved in dilute HCl and the solution treated according to the Zimmermann-Reinhardt method#.

(Treadwell and Hall "Analytical Chemistry" Vol.II P. 607)

The sulphate was determined by the usual method of precipitation with Barium Chloride in acid solution, allowing to stand twelve hours, then filtering through a weighed Gooch, dried and weighed. Five gram sample was used.

Carbonates were determined using Parr's Total Carbon apparatus. The Carbon Dioxide evolved on the addition of dilute HCl and subsequent heating to boiling was absorbed in NaOH and c.c's absorbed noted. Barometer pressure and temperature at the time of the operation was also noted. From Parr's Total Carbon table the factor used was obtained.

Calculations:

$$\frac{\text{Factor} \times \text{c.c's absorbed} \times 1000 \times 100 \times \text{atomic wt. of } NaHCO_3}{\text{wt. of sample} \times \text{atomic wt. of C.}} =$$

$$\% \ NaHCO_3$$

Free sulphur was obtained by extraction with Carbon Disulphide by means of a Soxhlet extractor and then evaporating off the Carbon Disulphide, leaving the pure sulphur which is weighed directly.

Moisture was determined in the usual way.

Results:

Moisture.....	.23%
Sodium Bicarbonate.....	.97%
Sodium Sulphate.....	2.73%
Sodium Chloride.....	94.98%
Free Sulphur.....	.25%
Ferric Oxide as Fe.....	.928%
	100.088%

Sample #6.

Sample #6 was similar to Sample #5. It was of the salt block type, and upon a qualitative examination the presence of sulphates, chlorides, free sulphur, carbonates, and ferric iron was shown.

Quantitative Methods.

The methods used in this analysis were the same as those used in Sample #5, so it will not be necessary to repeat the details of procedure.

The results of the analysis are as follows:

Ferric Oxide as Fe.....	1.30%
Sodium Bicarbonate.....	1.12%
Sodium Sulphate.....	8.38%
Sodium Chloride.....	88.03%
Free Sulphur.....	1.07%
Moisture.....	.68%
	100.58%

Sample #7.

Sample #7 was a liquid stock tonic. It was claimed to be a cure for worms, anemic condition, disability of the stomach, etc. The liquid was brownish in color, had a peculiar sweetish odor and a bitter taste. It was supposed to contain less than 2% Ferric Oxide.

Qualitative Tests.

A complete qualitative test was run on this sample with the result that sulphate, ferric and ferrous salts, silica and a volatile oil were found.

Quantitative Methods.

Iron was found to be present in both the ferric and ferrous state. The bottle was well shaken and 5c.c's were drawn out by means of a pipette, placed in a weighing bottle, and weight obtained. Since ferrous sulphate is soluble in a water solution, the sample was filtered, and filtrate oxidized with Bromine water, precipitated with Ammonia, precipitate re-dissolved in HCl and the Zimmermann-Reinhardt method followed. In this way the amount of ferrous iron was obtained. The ferric compound left as the insoluble matter on the filter paper was completely dissolved in HCl, and the Zimmermann-Reinhardt method was also used in this determination. Total sulphate was then determined by the usual method with Barium Chloride. Since part of the iron was present in the sample as ferrous sulphate, it was simply a matter of calculation to obtain the percentage of Ferrous Sulphate. Sodium Sulphate was also present in the tonic and by means of subtracting the amount of sulphate used as Ferrous Sulphate from the total Sulphate gave the amount of sulphate present as Sodium Sulphate.

The amount of Silicate present was determined by weighing out a definite amount of the solution and filtering. The insoluble matter on the filter paper was washed into a casserole and dilute HCl added. The solution was then evaporated to dryness on a steam bath until the Silica is completely dehydrated. It was then taken up with water and dilute HCl and filtered. The Silica and filter paper was then put in a crucible and paper burned off. Sodium Carbonate was added and the mixture fused for thirty minutes. The fusion was then dissolved in dilute HCl and again filtered. The Silica is now practically pure. The Silica with filter paper is placed in a crucible and after paper has been burned off, it is cooled and weighed. Then the Silica is covered with two or three c.c's of water, a drop or so of concentrated Sulphuric Acid added, and 5 c.c. of pure HF. It is then evaporated under a hood, at first slowly, and after all fumes have been expelled, it is finally heated over a blast lamp, cooled, and final weight taken. The difference between the two weights gives the amount of Silica present.

The quickest and easiest method of obtaining the volatile oil was found to be by steam distillation. Approximately seventy grams of the sample was weighed out and placed in a distilling flask and steam distilled until all the volatile oil came over in the receiving flask. The volatile oil was then completely extracted from the water solution with chloroform and the chloroform allowed to slowly volatilize off leaving the oil. Reference was then made to Allen's "Commercial Organic" for the determination and identification of volatile oils. Two methods were suggested: 1-specific gravity, 2-index

of refraction. The specific gravity was obtained by weighing in a small glass tube a certain amount of the oil against an exactly equal amount of water. The specific gravity of the oil was found to be approximately 1.072 at 25°C. The index of refraction of the oil was next determined and it was not easy to get a correct reading, but at 25°C. the index of refraction was between 3 and 4. The oil corresponding to this data was oil of sassafrass. It was also recognized by its characteristic odor.

The small amount of free sulphur obtained was in all probability due to the decomposition of the Carbon Disulphide used.

The specific gravity of the tonic was then obtained by weighing a definite amount of the solution against an exactly equal amount of water and applying the specific gravity formula.

The following results were obtained:

	% by weight	% by volume
Ferrous Sulphate.....	1.38 %	1.43 %
Sodium Sulphate.....	.72 %	.74 %
Ferric Oxide.....	.081%	.084%
Oil of Sassafrass.....	.55 %	.57 %
Silica.....	.40 %	.41 %
Free Sulphur.....	.09 %	.097%
Water.....	96.779%	96.669%
Total.....	100.00 %	100.00 %

Specific Gravity.....1.0290.

Sample #8.

Many of the stock cures at present on the market have for their main ingredient many species of seeds and roots. The most common seeds and roots that are used are the different varieties of wormseed, such as the Levant wormseed, American wormseed, May Apple root, Poke root, Quassia, Gentian, Tobacco, etc. The Levant wormseed contains the valuable Santonin, an inner lactone with the chemical formula $C_{15}H_{18}O_3$. However, when the seed is added to the stock tonic, it is very nearly desantoninized. Thus the seed not containing the Santonin is practically worthless as far as medicinal value is concerned. Some tonics advertise Santonin as the principle ingredient. Santonin has a high medicinal value on account of its ability to expell all forms of intestinal worms if taken in sufficient quanties. Its high cost prevents its use in tonics in any large amounts. Accordingly, K. Thaeter's method of extraction of Santonin from wormseed was used#.

(Autenrietn and Warren "Detection of Poisons" P. 273)
This method calls for the extraction of the Santonin with absolute alcohol, using the Soxhlet extractor for twelve hours. The alcohol is then evaporated off and the white residue boiled with lime water to form Calcium Santoninate. Filter while hot and wash the residue with water. Faintly acidify the filtrate with Sulphuric Acid and warm gently until Santonin crystals begin to form. Then add 100 grams of Aluminium Acetate solution (dissolve 300 parts of Aluminium Sulphate in 800 parts water; add Acetic acid (specific gravity..1.04) 360 parts; triturate 130 parts Calcium Carbonate with 200 parts water, and add this mixture slowly and with constant stirring to the

first solution, allow to stand twenty four hours, and filter. Use filtrate.), heat the mixture to boiling and finally evaporate to dryness on water bath. Mix the finely powdered residue with three grams of MgO, moisten a little with water and bring quickly to dryness. Powder the residue, dry at 105°C. and extract in a Soxhlet with anhydrous ether for five hours. Santonin is deposited upon distilling the ether as a faintly yellowish residue which is then dried at 100°C. to a constant weight. On account of the small amount of Santonin in the sample and the errors liable to be made in the working out of the method, the quantitative determination of Santonin was omitted.

The tonic was then tested for other chemicals. A cathartic should be present to expell the worms destroyed by the Santonin. Calomel (HgCl) was found to be the necessary cathartic. It was decided that it would be best to determine the mercury present as metallic mercury#.

(Treadwell and Hall "Analytical Chemistry" Vol. II P. 171) Almost all mercury compounds are quantitatively decomposed on heating with lime according to the equation

$$HgX + CaO = CaX + Hg + O.$$

To carry out this determination, a glass tube 60cm. long and 1.5 cm. wide, open at both ends, is taken and in one end an asbestos plug is placed, followed by eight cm. of pure lime, then an intimate mixture of a weighed amount of substance with lime, finally a layer of lime about 30cm. long and at the other end of the tube another asbestos plug. After the tube has been filled, the end nearest this second plug is drawn out until only

4 cm. wide, and is connected by means of rubber tubing to a Peligot tube. In absence of any Peligot tube, a weighed U-tube was used. In the other part of the U-tube, gold leaf was placed. The glass tube was placed in a combustion furnace and illuminating gas passed through for a half hour. Finally the tube was slowly heated, first where the 30 cm. of lime was. During the whole of the operation, illuminating gas was passed slowly through the tube. The mercury condensed in the U-tube, but also much water from the lime and resin from the seed present were collected in the tube making a correct weight impossible. Also a small amount of mercury collected in the drawn out end of the glass tube. It was decided the best thing to do in this case was to dissolve the mercury in aqua regia. Accordingly, the mercury in the U-tube and that in the end of the combustion tube was dissolved by aqua regia and then evaporated to dryness on the steam bath. A few c.c's more of aqua regia was added and solution washed with dilute HCl into a weighed beaker. It was brought to dryness twice and then weighed as mercuric chloride. The factor $\frac{HgCl}{HgCl_2}$ x wt. of $HgCl_2$ x 100 divided by sample, gave the percent of mercuous chloride.

The other substance in the sample was the seed itself, and a carbonate. It could not be determined whether the Santonin was in the seed or if it had been put in and mixed with the seed. In all probability, seed containing Santonin was placed in the tonic and then the HgCl and $NaHCO_3$ and the seed pressed together into the tablet-like samples.

The last substance to be found was carbonates. The

amount present was found by using Parr's Total Carbon apparatus the details of which were given under Sample #3.

The results of this analysis are as follows:

Insoluble Matter.....	37.82%
Sodium Bicarbonate.....	53.25%
Mercurous Chloride.....	9.33%
	100.40%

List of ingredients in stock tonics analysed and medicinal value of each.

1. Iron as Ferrous Sulphate. Of high medicinal value, especially valuable as a blood builder, supplying the Iron necessary for the blood cells.

2. Iron as Ferric Oxide. Of medicinal value, probably forms Ferric Chloride on reaction with the HCl of the stomach, thus supplying iron to the blood cells.

3. Sodium Sulphate or Glauber Salts. Its chief use is as a laxative. Should always be given in water solution.

4. Charcoal. Used mainly as a stomach sweetner and cleanser.

5. Sodium Bicarbonate. Perhaps its chief use is as a stomach sweetner, neutralizing the excess acid often formed in the stomach. It is also often used as a mild laxative.

6. Santonin. Noted for its ability to expell all forms of intestinal worms. Of high medicinal value when used in proper amounts. It is the chief constituent of Levant wormseed.

7. Mercurous Chloride or Calomel. Chief use is as a cathartic. It has a quick and positive action on the bowels. It is often used along with Santonin or other worm destroyers to get rid of the dead worms.

8. Free Sulphur. Laxative, diaphoretic and resolvent. It is supposed to be rendered soluble by the alkali of the bile. Supposed to be a blood purifier.

9. Oil of Sassafrass. Of no real medicinal value. Its chief use, similar to licorice, is to give the tonic a pleasant flavor. In large quantities, it acts as a narcotic.

10. Silica. Of no known medicinal value. Regarded simply as a filler to give weight to the tonic.

11. Sodium Chloride. Acts in small doses as a stomachic tonic; in larger ones as a purgative. Its most common use, however, is as an appetizer.

12. Magnesium sulphate or Epsom salts. Used mainly as a laxative.

13. Quassia Root. Has the property of simple bitters. It is purely tonic, invigorating the digestive organs, with little excitement of the circulation or increase of animal heat. Useful in failure of appetite. Also helpful in constipation.

14. Gentian Root. Excites the appetite and invigorates the indigestion. Helps many stomach ailments.

15. Tobacco. Often used in tonic because of the fact that intestinal worms are destroyed after eating the tobacco leaf. Must be given in rather large amounts to have any effect.

III Discussion of Results.

Inspection of the various analysis which were carried out will show that substances like iron, salt, charcoal, free sulphur, and sodium sulphate are present in the majority of the stock tonics of the three types analysed. In the majority of cases, the standard methods of analysis were applicable and gave accurate results. Inspection of the results will also show that the ingredients of the highest medicinal value were to be found in small quantities, while fillers which have no medicinal value, such as silica, spent wormseed, or a non-medicinal seed, were often added to give the substance weight. In all cases except those in which the moisture content was less than one percent, the results were calculated on a dry basis.

IV Summary.

Three general types of tonics were analysed. The powder type, Samples #1, 2, and 3, usually contained Charcoal, Iron, Free Sulphur, Sodium Sulphate, Silica and Salt. In the salt cake type, Samples #4, 5, and 6, the most common constituents are Salt, Iron and Sodium Carbonate. The liquid type usually has water as a solvent to a large percentage. Other substances contained in the liquid form are similar to those of the salt block and powder type. Sample #7 is a fair example of the liquid type.

It has been shown that the standard methods of analysis can be used in nearly all cases with accurate results and a saving of time. Many of the tests are of a simple nature and can be quickly and accurately applied for a rapid metnod of analysis.

The microscope was used to a good advantage in detecting and determining the presence of seeds, roots and barks present in the tonic.

A list of medicinal values of the various ingredients was prepared in order to obtain an idea of the substances of the highest value. It was found that the substances of the best medicinal value were found to be present in small quantities, in some cases too small to be of any value as a tonic.